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Construction and calibration of equipment for obtaining heat capacity data at high temperatures

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CONSTRUCTION AND CALIBRATION OF EQUIPMENT FOR OBTAINING HEAT CAPACITY DATA AT HIGH TEMPERATURES

A Thesis

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Master of Science

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by

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INTRODUCTION

This is a study of the heat capacity of substances at high temperatures as determined by means of drop-calorimetry. The heat capacity may be defined as the quantity of heat required to raise the temperature of a substance by 1° C. This can be expressed as $C = \frac{Q}{T_2 - T_1}$. The concept of heat capacity is used in connection with a certain defined path such as those of constant volume or constant pressure. The following definitions apply: $C_v = \left(\frac{\partial E}{\partial T}\right)_v$ = heat capacity at constant volume and $C_p = \left(\frac{\partial H}{\partial T}\right)_p$ = heat capacity at constant pressure, where E = the internal energy, H = enthalpy and H and E are related by $H = E + PV$.

The heat capacity function is dependent upon the quantity of matter present and therefore can be expressed as the molar heat capacity in calories mole^{-1} degree^{-1} or in terms of specific heat as calories gram^{-1} degree^{-1}. In this work the molar heat capacity will be used.

Great interest in the determining of exact heat capacities at definite temperatures arose as the results of the empirical rule of Dulong and Petit, which states that the atomic heat capacity of most solid elements measured at atmospheric pressure is about 6.4 calories degree^{-1}. Although a theoretical treatment of heat capacities in terms of partition functions is possible--see Wall (16)--experimental

determination is the only present method for exact values, especially at high temperatures. These measurements allow one to calculate a number of the following thermodynamic functions:

$$\text{Free energy function } \frac{F_T - H_{298}}{T} = \frac{H_T - H_{298}}{T} - S_T =$$

$$\frac{1}{T}\int_{298}^{T} C_p dT - \int_{o}^{T} C_p d\ln T$$

$$\text{Enthalpy function} \quad H_T - H_{298} = \int_{298}^{T} C_p dT$$

$$\text{Entropy increments} \quad S_T - S_{298} = \int_{298}^{T} C_p d\ln T$$

By the use of these functions and the heat of formation data at 298° K, one may calculate the change of free energies, heats, and entropies for reactions at elevated temperatures.

DROP METHOD OF CALORIMETRY

The drop method used in this experiment was employed for the determining of heat capacity data because of its application to high temperature work. Adiabatic or isothermal conditions can be used in this method. For this work isothermal conditions were accomplished by the use of a metal block calorimeter.

The sample was placed in a platinum-10 per cent rhodium capsule that was suspended in a vertically mounted resistance furnace by nichrome wire. Since this work had a maximum temperature of 1000° C. there was no problem of melting or oxidizing the suspension wire. At higher temperatures platinum-rhodium wire must be used.

The furnace was separated from the calorimeter by means of a table top, transite insulation, water gate, and a solid copper gate. The sample was dropped into the center of an approximately fifty pound copper block that was nickel plated. The calorimeter was filled with an inert gas and was surrounded by a constant temperature bath. The temperature rise due to the heated sample was measured by means of a thermistor in conjunction with a Wheatstone bridge.

One of the main disadvantages of this method is the possibility of a metastable state for the sample due to sudden cooling after the drop. This problem may be solved by the use of a heat of solution calorimeter if the sample is water soluble.

CONSTRUCTION OF FURNACE

The furnace constructed for obtaining the high temperatures had the following specifications:

The total height was 15 1/4 inches with a width of 14 1/2 inches by 14 1/2 inches; top and bottom were made of 1/2 inch transite; furnace rested 1 5/8 inches above the table top which was protected by a 1/4 inch thick piece of transite and a fan that constantly blew the hot air away from the table; the central tube was a McDanel Zircotube which had an inside diameter of 3/4 inch and an outside diameter of 1 inch and was 21 7/8 inches long; two aluminum oxide bricks were located at the two ends of the central tube which was surrounded by six Norton Company silicon carbide "hot rods" which were 3/8 inch in diameter and 17 inches long with a 10 inch heating length; rods were surrounded by an aluminum oxide tube with an inside diameter of 2 inches and an outside diameter of 2 3/4 inches; bricks surrounding the furnace were Johns-Manville number 22 firebrick.

Each rod had a nominal resistance of 3.77 ohms and the unit was powered by a 20 amp Superior Electric Powerstat. The test amperage of the rods was approximately 20 amps with the test voltage at 70 volts. The rods were connected in three pairs. Two rods connected in series made a pair and the pairs were then connected in parallel. It was discovered that the Zircotube became conducting above 1500^{o} C. and shorted

out the heating elements. A 0 to 50 volt voltmeter and a 0 to 25 amp ammeter were connected into the circuit. This furnace can obtain temperatures up to 1500° C. but the calibrations have only been made to 1000° C.

FURNACE THERMOCOUPLE

A standard platinum versus platinum plus 13 per cent rhodium thermocouple was used to obtain furnace temperatures. The thermocouple was introduced from the top of the furnace with the junction located at the mid-point of the capsule. A Dewar flask directly above the furnace contained ice-water mixture for the cold junction.

The calibration of thermocouples may be done by one of the two following methods: calibration at fixed points or calibration by comparison with a standard instrument such as another thermocouple or resistance thermometer. In this work the thermocouple was calibrated at fixed points. According to the National Bureau of Standards Circular 590 a platinum versus platinum-rhodium thermocouple may be used in the temperature range of 0° C. to 1100° C. with an accuracy of 1° C. at any point when calibrated by this method.

The assigned primary points of the freezing point of ice (0° C.) and that of gold (1063.0° C.) along with the determined secondary points of the freezing of tin (231.9° C.), zinc (419.5° C.), and antimony (630.5° C.) were used.

The gold point was obtained by fastening a small piece of gold wire between the platinum and platinum-rhodium leads and observing the emf value at the point where the gold melted in the furnace. The other freezing points were obtained by

immersing the thermocouple in the molten metal according to the method outlined in the National Bureau of Standards Circular 590. A Hevi-Duty electric furnace was used as the source of heat. Care was taken to insure that oxidation of the metals did not occur. This was accomplished by covering the metals with a heavy layer of graphite.

All emf values were obtained by the use of a Leeds & Northrup K3 potentiometer. The galvanometer posts 400 and 2000 were connected and the guard posts W_1 and W_2 were connected in order to obtain readings in the millivolt range.

The observed values of emf at the calibration points are given in Table I. Graph I is a difference curve for the platinum versus platinum plus 13 per cent rhodium thermocouple, using the Standard Conversion Table for Leeds & Northrup Thermocouples.

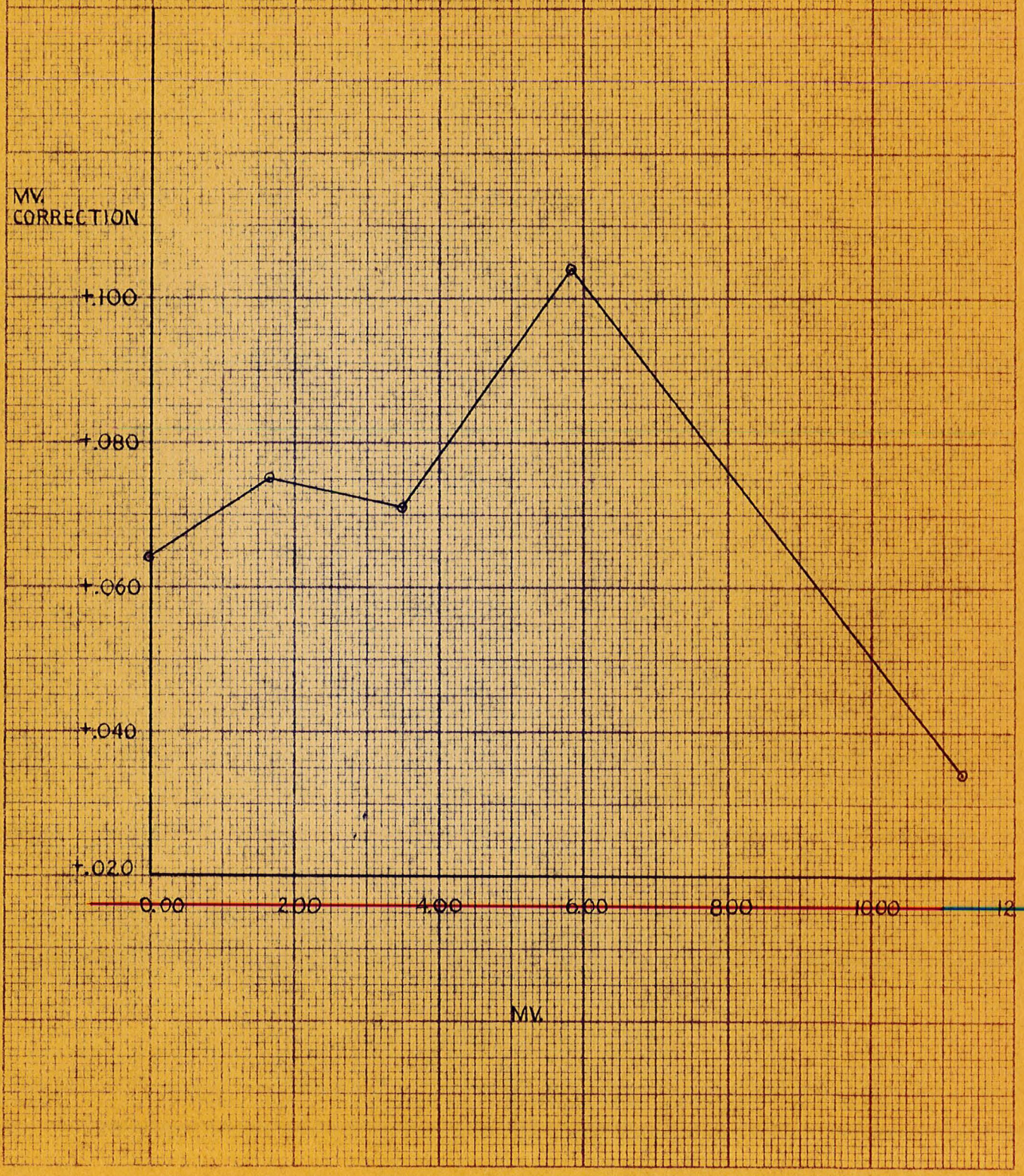
TABLE I

DATA FOR CORRECTION OF THERMOCOUPLE

Material	Temperature ^{o}C	Temperature ^{o}K	True EMF (mv.)	Observed Value (mv.)	Correction (mv.)
Ice + H_2O	0	273.2	0	-.064	+ 0.064
Sn	231.9	505.1	1.750	1.675	+ 0.075
Zn	415.9	692.7	3.599	3.528	+ 0.071
Sb	630.5	903.7	5.911	5.807	+ 0.104
Au	1063.0	1336.2	11.310	11.276	+ 0.034

GRAPH I

CORRECTION FOR Pt vs. Pt + 13 % Rh THERMOCOUPLE



SAMPLE CAPSULE

The sample capsule used for heating to high temperatures was made from five-thousandths inch sheet platinum-10 per cent rhodium alloy. Figure I shows the specifications. It was not necessary to seal the capsule for the calibration with synthetic sapphire because of the low vapor pressure, nonhygroscopic, and inert character of this material. For other more reactive substances the stem of the capsule must be fused shut. For the replacing of a sample the end of the stem is cut and fused shut again.

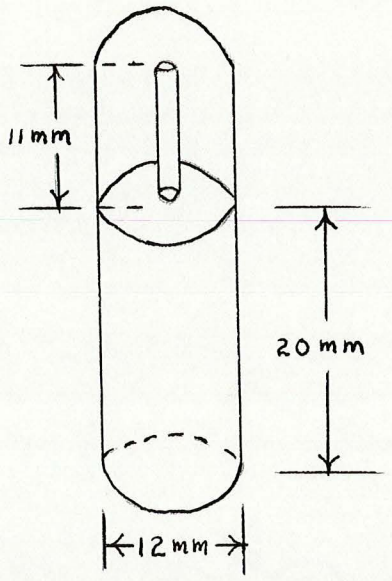


FIGURE 1

CONSTRUCTION OF CALORIMETER

The calorimeter that was used in this research had the following specifications:

The outside box was 21 inches high by 25 inches square and made of 1/2 inch plywood; the box cover was insulated with soft felt of 1 1/4 inches thickness, the cover thickness was 1 1/2 inches with a lip to fit over the box snugly; between the box and the outside can fiberglas insulation was used; the constant temperature can was 18 1/2 inches deep by 18 1/4 inches in diameter; the calorimeter jacket was supported 3 1/2 inches above the bottom of the constant temperature can by a three legged steel stand of adjustable height.

The bath fluid used was Diala AX transformer oil that was agitated rapidly by means of two stirrers. The location of the stirrers and other parts is illustrated in Figure 2. One stirrer was a large blade type while the other was a belt driven model consisting of two four blade propellers on a shaft, housed in a brass tube that was 14 inches long and had a diameter of 3 1/2 inches, with an integrally mounted bare wire nichrome heater in the lower part of the stirrer tube. This heater was powered by a powerstat transformer with the dial set at 30 nominal volts.

An auxiliary heater was used to bring the bath to operating temperature. Constant temperatures with a deviation

of less than five-thousandths of a degree were obtained by means of a water cooled copper coil in conjunction with the heater. A constant flow of water was maintained by the use of a constant water head device made from a three necked flask. This is necessary because of the variation of the water pressure from the faucet. A mercury thermo-regulator was used in conjunction with a model E-2 Emil Greiner Company electronic relay. Bath temperatures were measured with a Beckmann thermometer set with a range of 25.0° C. to 30.0° C.

All details concerning the water gate, calorimeter jacket, diagram of the calorimeter, and electrical heater in the copper block may be found in Grimley's thesis (3). The various sizes of conductor wire used in this work corresponds to Grimley's specifications (8).

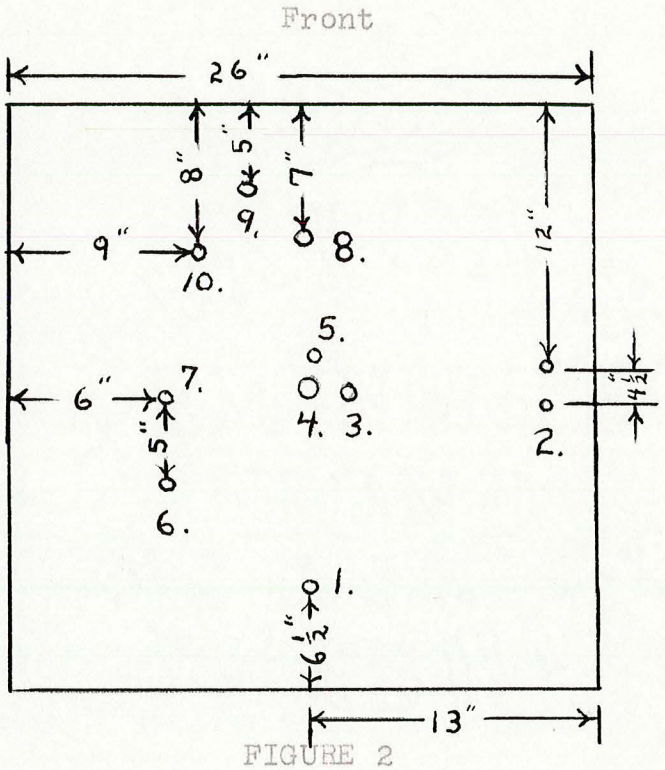


FIGURE 2

TOP VIEW OF CALORIMETER

1. Auxiliary heater (optional)
2. Copper coil for cooling water
3. Rod connecting copper gate with water gate directly above calorimeter
4. Hole for sample capsule
5. Calibration heater wires and thermistor leads
6. Small heater and stirrer
7. Thermo-regulator
8. Large stirrer
9. Beckmann thermometer
10. Large heater

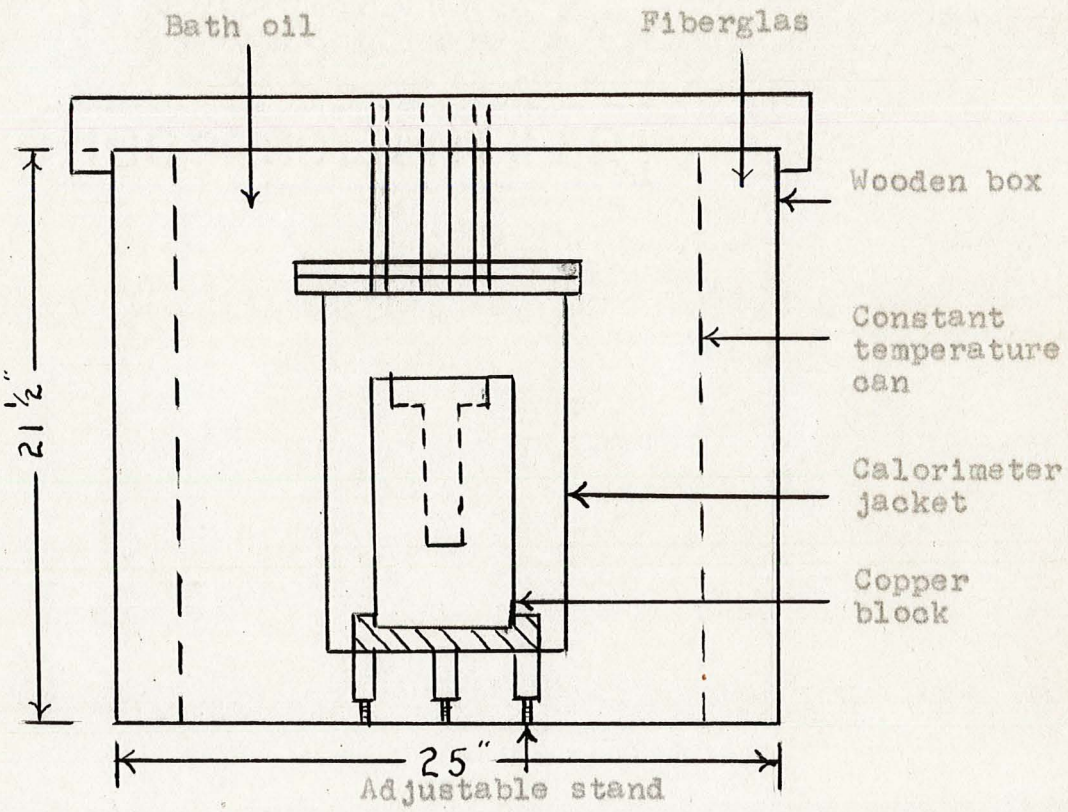


FIGURE 3

SIDE VIEW OF CALORIMETER

THERMISTOR

The temperature sensing device used in the copper colorimeter block was a thermistor. Thermistors are non-linear elements of high negative temperature coefficient. The equation for the resistance of a thermistor as a function of temperature is the following: $\log R = \log R_o + \frac{B}{2.303}\left(\frac{1}{T} - \frac{1}{T_o}\right)$ where R = resistance (ohms) at temperature T (degrees Kelvin), R_o = resistance (ohms) at temperature T_o (degrees Kelvin), and B (degrees Kelvin) = a constant for a given thermistor over a wide temperature range. Over a very small temperature range, in this case 1° C., a fairly linear resistance to temperature curve may be obtained. The circuit used for measuring resistance changes of the thermistor was a wheatstone bridge.

One arm of the bridge was a Western Electric 14B, bead-type, 2000 ohms thermistor. The balancing arm consisted of a General Radio Company 5-decade resistance box, variable in 0.1-ohm steps from 0.1 to 11,111.0 ohms. Two manganin wire wound resistors of 2000 ohms nominal resistance were the other two arms. A 6 volt storage battery was the source of potential with two resistors of 750 K ohms in parallel and a 15K ohms resistor in series to serve as a voltage dropping device. The bridge was used in conjunction with a Leeds & Northrup type HS galvanometer. The current was kept

sufficiently small in order to prevent self-heating and readings were taken with the circuit closed for only a few seconds. The thermistor was coated with a layer of Glyptal varnish and placed in the block.

Calibration of the thermistor was accomplished in the following manner. An auxiliary bath was made from a large glass tank filled with transformer oil and insulated with a cotton jacket. A temperature difference of $\pm$ 0.001° C. was maintained by using a cooling coil, heater, stirrers, and thermoregulator in the same manner as used for the calorimeter bath. The copper block was placed in the bath and a Beckmann thermometer placed in the hole in the center of the block that was filled with mercury to insure rapid heat transfer. The bath and the block were allowed to come to equilibrium and after an hour the resistance and temperature readings were recorded. Readings at 0.1° intervals over the range of 25° C. to 30° C. were taken. The results of this calibration are shown on graphs II-VII. All Beckmann readings have been corrected according to the National Bureau of Standards Certificate for this particular liquid-in-glass thermometer. After the calibration of the thermistor was completed the copper block was placed in the calorimeter jacket and none of the circuit was changed.

It has been observed by McMullan (9) that in the application of thermistors to temperature measurements there

is a slow change in resistance over a period of time. This problem was eliminated by the fact that once the thermistor was placed in the copper block it existed in essentially the same environment throughout the time of research and the current in the thermistor was held below 15 μ amp. Even with a gradual drifting of the thermistor resistance no great error would be introduced in this calorimetry work due to the fact that only differences in temperature were needed.

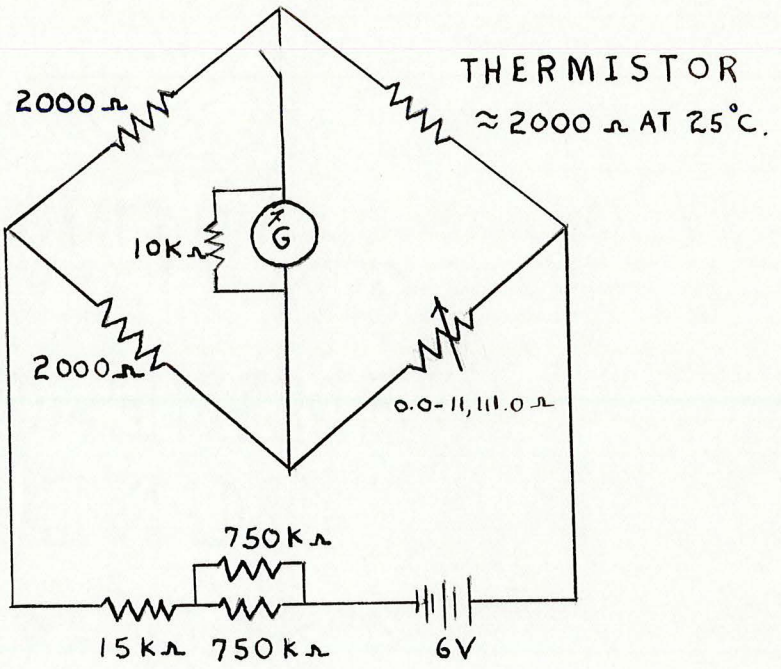


FIGURE 4

DROP CALORIMETER THERMISTOR CIRCUIT

OPERATING PROCEDURE

The purpose of this section is to describe the procedure used in the operation of the calorimeter throughout a run, either for calibration with a standard or obtaining heat capacity data for an unknown.

Procedure Prior to the Run

1. Turn on magnet powered by battery eliminator or storage battery and lift sample capsule into center of furnace.
2. Insert metal rod to hold plug and sample in place and then turn off magnet. This is necessary because of the heating of the magnet when turned on for any length of time.
3. Close water gate.
4. Turn on furnace. Voltage is supplied slowly at about three volts per hour until temperature is reached.
5. When the furnace is at the working temperature put crushed ice and water in the Dewer flask and connect the thermocouple to the potentiometer making sure that the thermocouple junction is at the middle of the capsule.
6. Turn on argon making sure that the flow through the sulfuric acid does not produce large bubbles that would flow into the system.

7. Plug in the galvanometer and connect the potentiometer to the power source. Allow an hour warmpup time. (Used in conjunction with thermocouple.)
8. Turn on the calorimeter stirrers.
9. Bring bath to operation temperature with the large heater.
10. Turn on the electronic relay which regulates the small heater.
11. Turn on the cooling water for the water gate and the calorimeter cooling coil.
12. Adjust the water by means of a pinch clamp to obtain regulation of the bath to $\pm 0.005^{\circ}$ C.
13. Adjust the initial temperature of the calorimeter so that large temperature gradiants are eliminated. It is desired to have an initial temperature of the block slightly below the bath temperature and a final temperature slightly above. The copper block may be heated by turning on the heating coil used in calibration or cooled by dropping dry ice in at the water gate.
14. Allow the capsule to come to equilibrium with the furnace temperature. For an empty capsule this was only a few minutes while for a capsule that contained a sample at least an hour was allowed.

Procedure During the Run

1. Turn off argon.
2. Make sure bath is regulating properly.
3. Start timer.
4. Obtain emf readings for the thermocouple to insure that the furnace is holding constant. Be sure that ice and water are throughly mixed.
5. Obtain initial calorimeter readings with the thermistor circuit. Several readings should be made in order to obtain data for gradual heating of copper block.
6. Open water gate.
7. Drop capsule. This was originally designed to be done by means of gravity but much trouble was experienced because of bending of the wire due to the fact that the metal plug dropped faster than the capsule. This was especially true with the empty capsule. The capsule in this work was dropped in the following manner: The magnet was turned on and the metal rod holding the plug in the tube was removed. The magnet was then manually lowered as quickly as possible.
8. Close water gate.
9. Turn off magnet.
10. Obtain resistance readings about every minute throughout period of increasing temperature.

11. Obtain several resistance readings about every minute as temperature of block decreases.

Procedure After the Run

1. Disconnect the galvanometer, potentiometer, and timer.
2. Turn off stirrers.
3. Turn off electronic relay and heater.
4. Turn off water.
5. Turn off furnace. This was only done when a certain set of experiments had been completed. The furnace may be left on for weeks without any harm. When the furnace is turned off it is done by the reverse method that it was initially heated, i.e., by small steps.

CALORIMETER CALIBRATION

In isothermal calorimetry the time temperature curve is divided into three periods: the initial period, the reaction period, and the final period. In the calculation of the heat gained in the copper block one assumes that Newton's law is valid. The theoretical derivation of this law--see Grimley (3)--gives the following results:

$$\Delta T = T_f - T_i - \left(\frac{dT}{dt}\right)_i (t_m - t_i) - \left(\frac{dT}{dt}\right)_f (t_f - t_m)$$

T = temperature

t = time

i = initial

f = final

t_m = mid-time

For this work the numerical method of determining T was used. The theoretical derivation of this method--see Kubaschewski & Evans (5)--gives the following results:

$\Delta T = T_f - T_i$ + correction, where the correction =

$K\Sigma (T^1 - T_i) - m_i Z$

Z = number of readings in the reaction period

$K = \frac{M_i - M_f}{T_f - T_i}$ = constant in Newton's law of cooling for the apparatus

M_i = rate of change of temperature in initial period

M_f = rate of change of temperature in the cooling period

T^1 = mean of consecutive temperature readings in the reaction period

Calibration of the calorimeter was done electrically with a check obtained by using a sample of a-Al_2O_3. The National Bureau of Standards prepares pure samples of this material to serve as a heat capacity standard. The procedure and circuits used for the electrical calibration corresponds exactly with the method outlined by Grimley (3); his discussion of calibration errors would therefore apply to this calibration.

In the electrical calibration each run had exactly the same temperature range. The change in heat capacity of the block was assumed to be negligible over the small temperature range used. In the work done by Grimley (3) it was shown that this assumption introduces less than 0.4 per cent error.

TABLE II

SAMPLE CALCULATION FOR ELECTRICAL DETERMINATION OF HEAT CAPACITY OF COPPER BLOCK CALORIMETER (EXPERIMENT III)

Time (sec)	Thermistor Resistance Readings (ohms)		Initial Period T* °C	Δ T °C
0	2037.8		2.123	0.000
50	2037.8		2.123	0.002
100	2037.7		2.125	0.002
150	2037.6		2.127	0.003
200	2037.5		2.130	0.002
250	2037.4		2.132	0.002
300	2037.3		2.134	0.0018 Mean

				Reaction Period	
			T °C	T' °C	T' - T_i °C
300	2037.3	T_i	2.134	2.178	0.044
350	2031.5		2.213	2.338	0.204
400	2014.2		2.462	2.608	0.474
450	1994.4		2.755	2.905	0.771
500	1974.0		3.055	3.222	1.088
550	1950.5		3.390	3.562	1.428
600	1927.6		3.734	3.853	1.719
650	1911.8		3.972	4.034	1.900
700	1904.0		4.095	4.124	1.990
750	1900.1		4.154	4.167	2.033
800	1898.5		4.180	4.184	2.050
850	1898.0		4.187	4.191	2.057
900	1897.5	T_f	4.195		Σ 15.758

Z = 12

*T values obtained from thermistor calibration graphs - Beckmann readings.

TABLE II (continued)

Time (sec)	Thermistor Resistance Readings (ohms)	Final Period T °C	Δ T °C
950	1897.5	4.195	-0.007
1000	1897.9	4.188	-0.003
1050	1898.1	4.185	-0.002
1100	1898.2	4.183	-0.003
1150	1898.5	4.180	-0.004
1200	1898.7	4.176	-0.0038 Mean

Calculations:

$T_f = 4.195$ $\quad M_i = 0.0018$

$T_i = \underline{2.134}$ $\quad M_f = \underline{-0.0038}$

$T_f - T_i = 2.061$ $\quad M_i - M_f = 0.0056$

$$K = \frac{M_i - M_f}{T_f - T_i} = \frac{0.0056}{2.061} = 0.00272$$

Correction:

$$\Sigma(T' - T_i)K - M_i Z = (15.758)(0.00272) - (.0.0018)(12)$$

$$= 0.0428 - 0.0216 = 0.0212$$

Value + correction = 2.061 + 0.021 = 2.082 °C.

GRAPH II

EXPERIMENT III

ELECTRICAL CALIBRATION

RESISTANCE VS. TIME

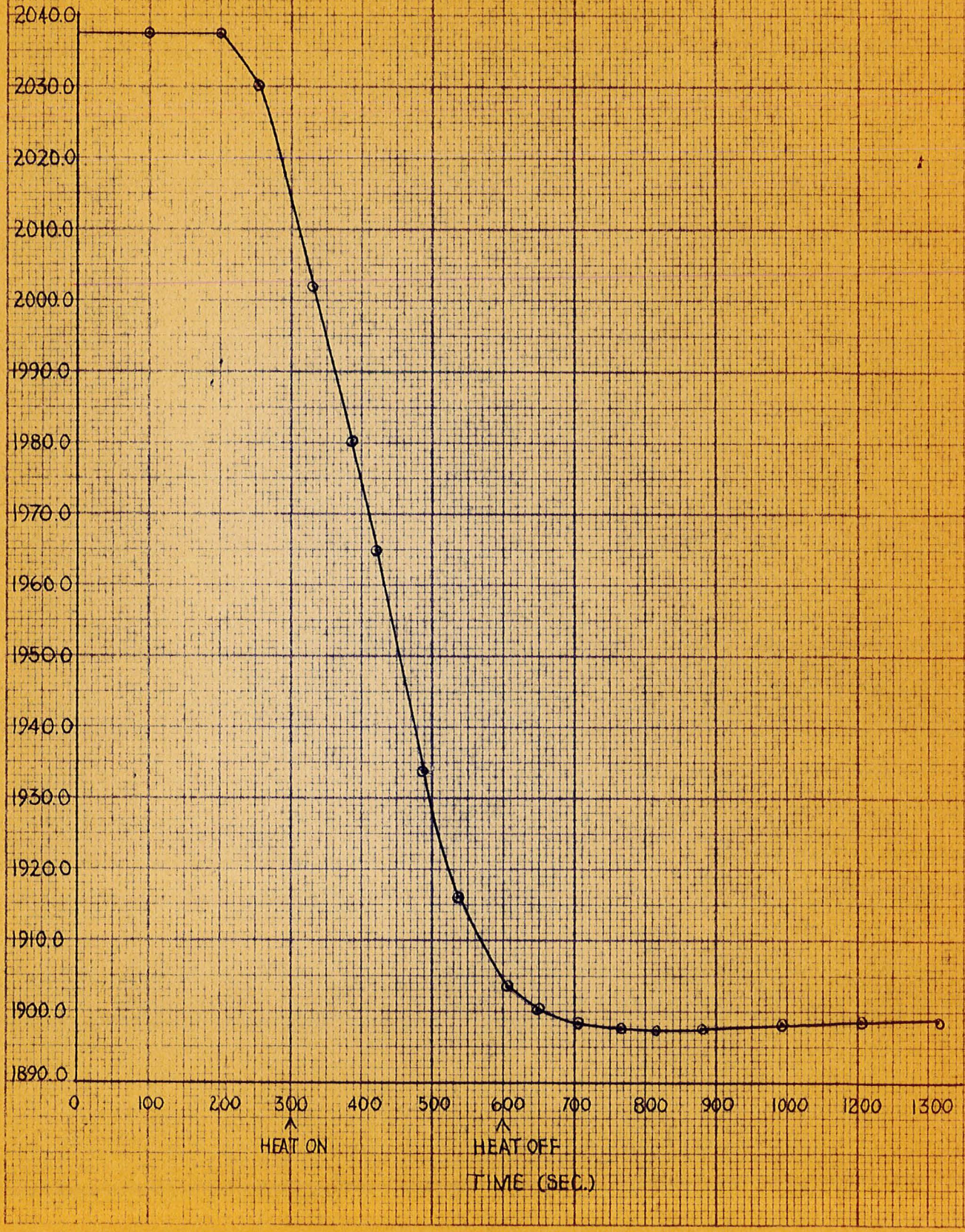


TABLE III

ELECTRICAL CALIBRATION RESULTS

Experiment	Corrected ΔT	i (amps)	E (volts)	time (sec.)	Initial Temp. °C
I	1.994 °C.	2.507	22.49	300	27
II	1.945 °C.	2.491	22.36	300	27
III	2.082 °C.	2.565	22.97	300	27
IV	1.992 °C.	2.522	22.55	300	27

Heat Capacity of Copper Block Calorimeter $P = \frac{Eit}{\Delta T\ 4.184 \Delta T}$

I	2.027×10^3 cal/o
II	2.053×10^3 cal/o
III	2.029×10^3 cal/o
IV	2.047×10^3 cal/o
	2.04×10^3 cal/o Average

TABLE IV

AVERAGE VALUES FOR EMPTY CAPSULE

EMF m(-volts)	Corrected EMF m(-volts)	°C	Temperature °K	Δ R (ohms)	Δ T °C	$C_p\Delta T$ $H_T - H_{300}$
1.558	1.632	219	492	1.1	0.015	30.6
2.506	2.579	319	592	1.5	0.021	42.8
3.476	3.547	414	687	2.35	0.033	67.4
5.269	5.365	583	856	2.9	0.041	83.6
5.940	6.043	642	915	3.55	0.048	97.9
8.410	8.418	845	1118	4.33	0.061	124
9.140	9.202	902	1175	4.63	0.065	133
10.456	10.499	1002	1275	5.4	0.076	155
11.840	11.867	1104	1377	6.1	0.086	175

Calculations for Equation of $H_T - H_{300}$

$$H_T - H_{300} = aT + bT^2 + c$$

Data points used:

T	$C_p\Delta T$
592	42.8
856	83.6
1275	155

Final Equation

$$H_T - H_{300} = 0.121T + 2.32 \times 10^{-5}T^2 - 36.9$$

TABLE V

$H_T - H_{300}$ RESULTS FOR EMPTY CAPSULE

T °K	$H_T - H_{300}$ (cal)	$H_T - H_{300}$ (cal/mole)	$H_T - H_{298}$ (cal/mole)
400	15.2	583	594
500	29.4	1126	1137
600	44.1	1690	1701
700	59.2	2268	2279
800	74.7	2862	2873
900	90.8	3479	3490
1000	107.3	4111	4122
1100	124.3	4763	4774
1200	141.7	5429	5440

Weight of Pt. + 10% Rh. capsule = 4.675 grams = 0.0261 mole

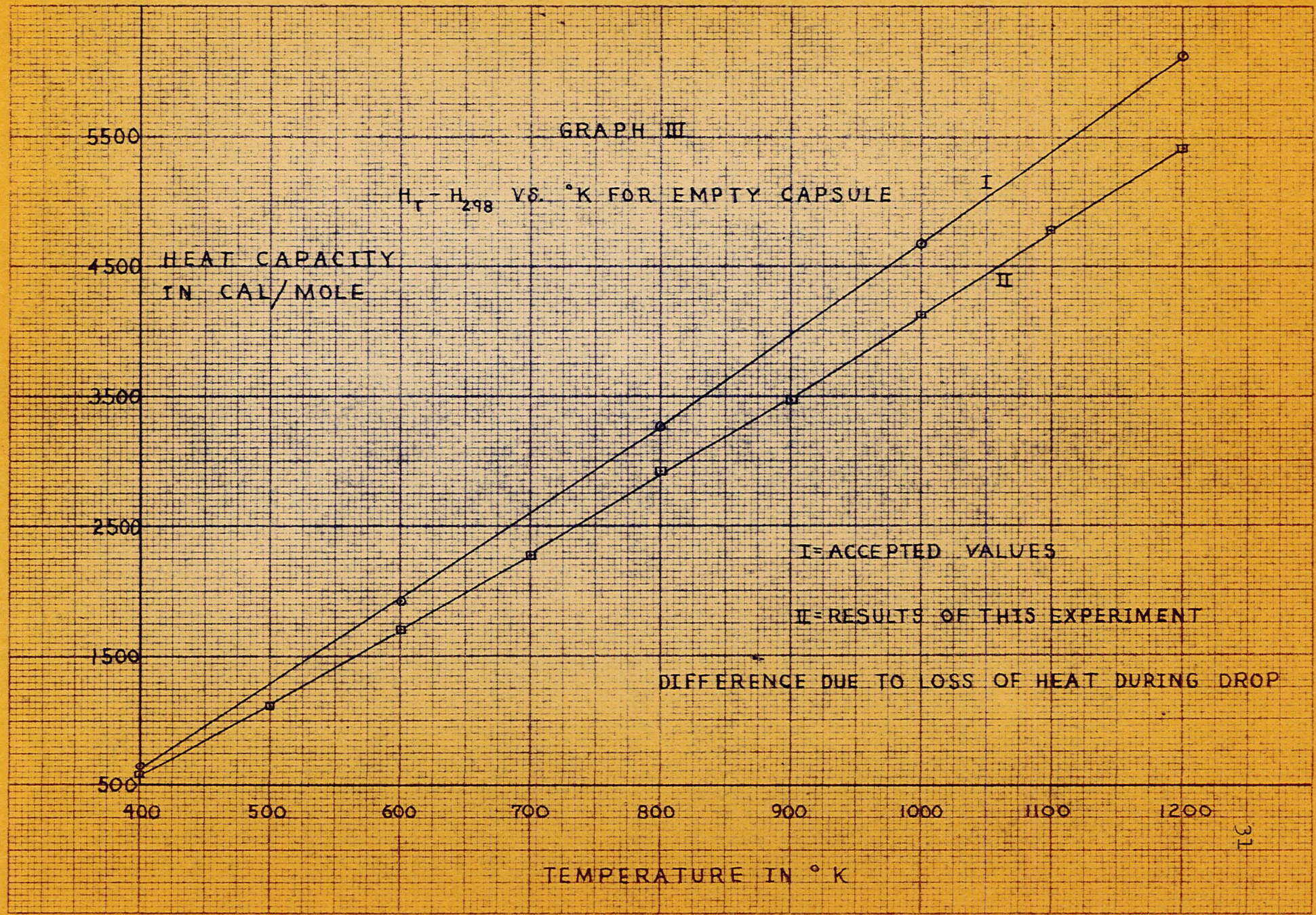


TABLE VI

AVERAGE VALUES FOR Al_2O_3 AND CAPSULE

EMF (mv.)	Corrected EMF (mv.)	Temperature °C	Temperature °K	Δ R (ohms)	Δ T °C	$C_P \Delta T$ $H_T - H_{300}$ (calories)
1.539	1.613	217	490	7.75	0.110	224.4
3.445	3.516	412	685	16.3	0.233	475.3
5.625	5.729	615	888	25.4	0.362	738.5
5.703	5.805	621	894	25.8	0.366	746.6
7.906	7.983	805	1078	35.6	0.503	1026
8.073	8.148	818	1091	35.9	0.512	1044
10.515	10.559	1006	1279	45.5	0.649	1324
10.605	10.648	1014	1287	46.6	0.670	1367

TABLE VII

HEAT CONTENT OF Al_2O_3

T (°K)	Al_2O_3 + Capsule H_T-H_{300} (cal.)	Capsule $H_T - H_{300}$ (cal.)	Al_2O_3 $H_T - H_{300}$ (cal.)	Al_2O_3 H_T-H_{300} (cal./mole)	Al_2O_3 H_T-H_{298} (cal./mole)	NBS value (cal./mole)	% Deviation
490	224.4	28.0	196.4	4474	4499	4287	+ 4.2
685	475.3	57.0	418.3	9531	9556	9584	- 0.3
888	738.5	88.9	649.6	14795	14820	15334	- 3.4
894	746.6	89.9	656.7	14959	14984	15502	- 3.3
1078	1026	120.4	905.6	20629	20654	20913	- 1.2
1091	1044	122.7	921.3	20986	21011	21305	- 1.4
1279	1324	169.5	1154.5	26298	26323	26990	- 2.5
1287	1367	170.7	1196.3	27255	27280	27225	+ 0.2

DISCUSSION

The fairly large and irregular deviations of this work as compared to that of the National Bureau of Standards for Al_2O_3 can be accounted for in the following manner.

The size of sample is definitely a factor to be considered in any work of this type. Because of the size of the capsule used, this work was done with a sample of only one-third the size used by Grimley (3). As a result the temperature of the copper block changed less than one degree. A sample large enough to cause a five degree temperature change would improve the accuracy.

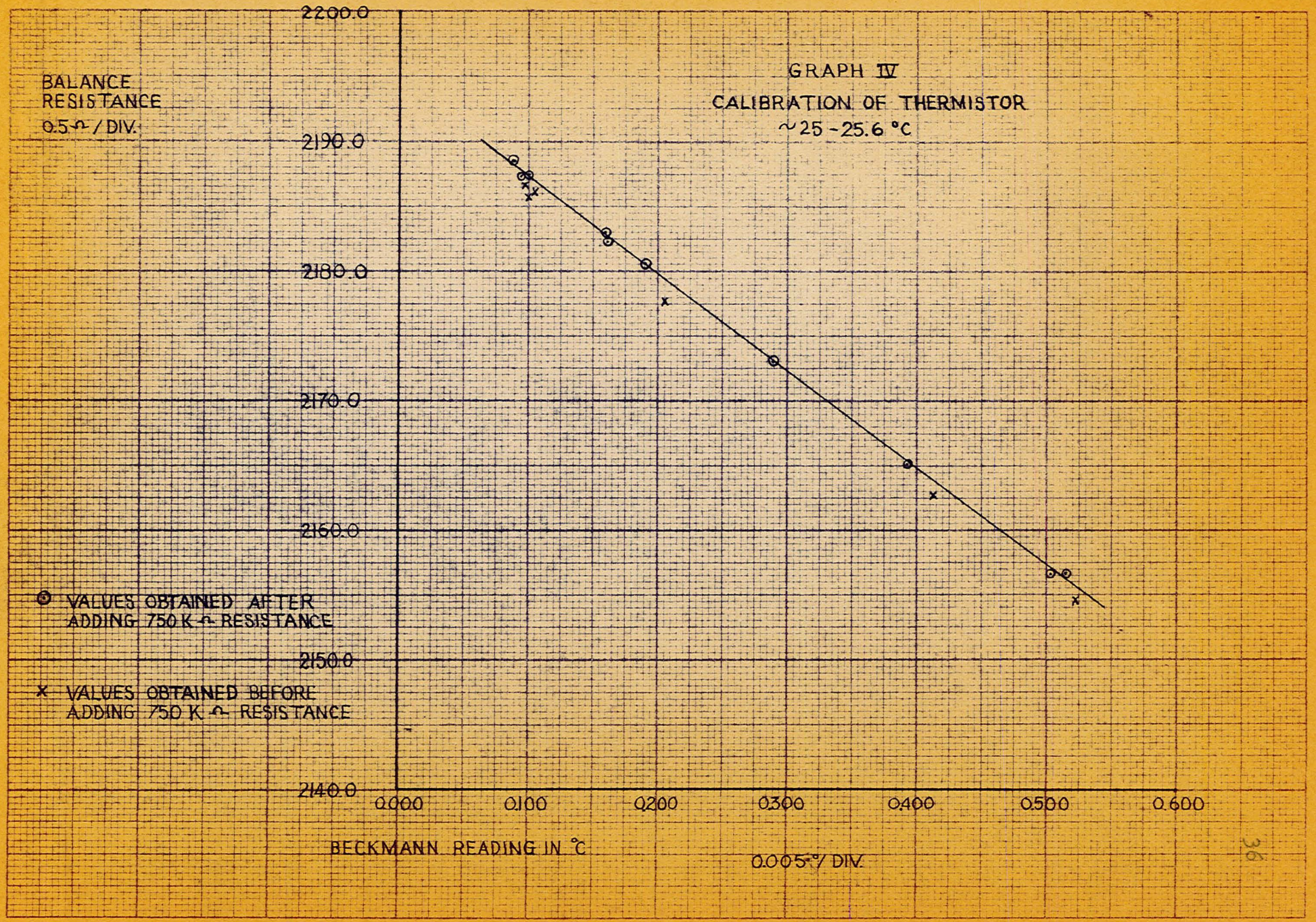
The thermal loss during the drop is corrected by experimentally obtaining heat capacity values of the empty capsule. In this work the capsule was manually lowered for each drop. Although an effort was made to make each drop exactly as the previous one, there was a difference in the time that the capsule left the furnace until the water gate was closed. A gravity drop system with the water gate and magnet release in conjunction with one another, as described by Margrave (8), would greatly reduce this error.

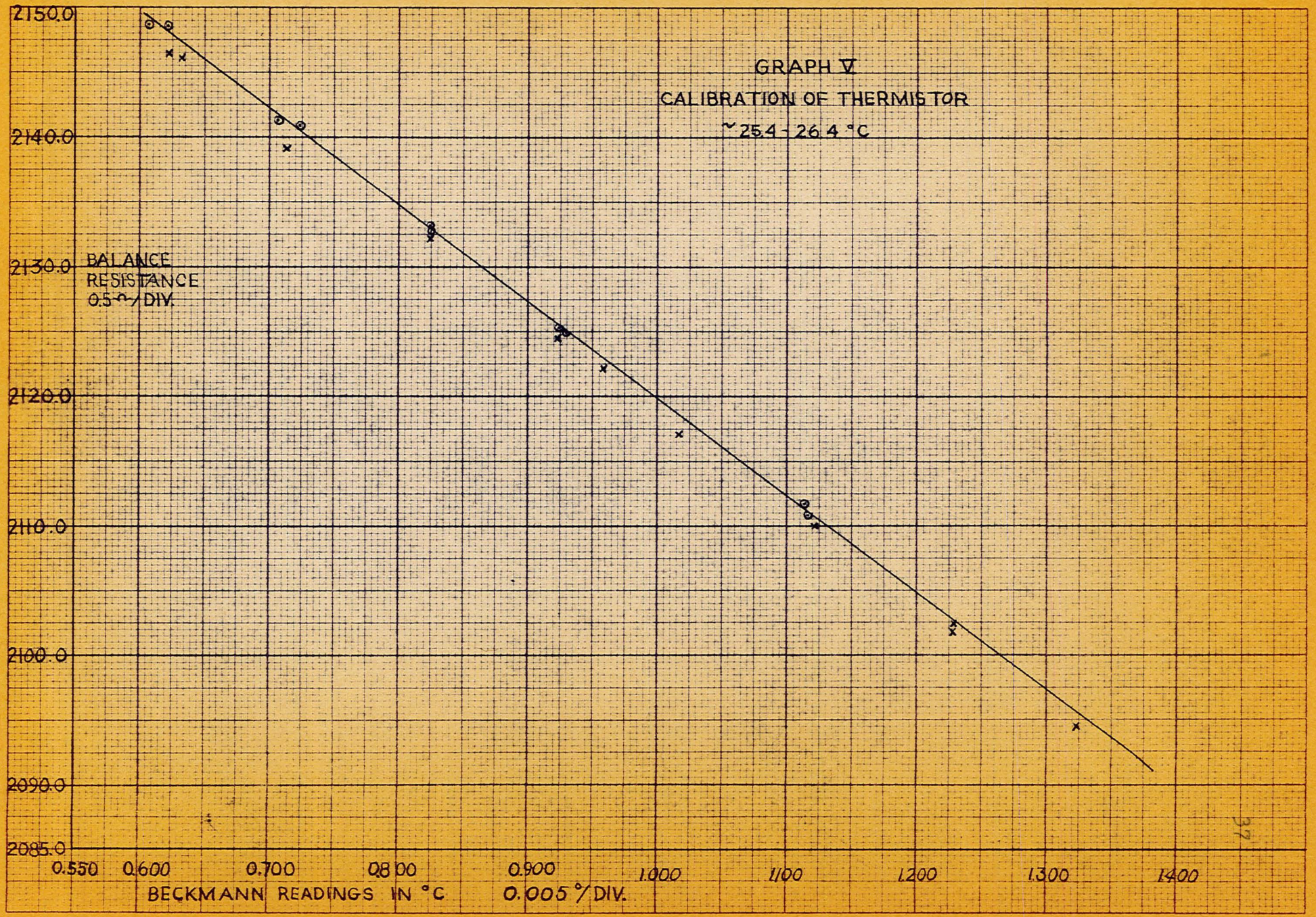
The thermocouple could have introduced an error by two different means. The first being the fact that the calibration of the thermocouple gave a rather large correction factor. Such a large correction (approximately 10° C. at one point) is irregular for a platinum-rhodium thermocouple, but

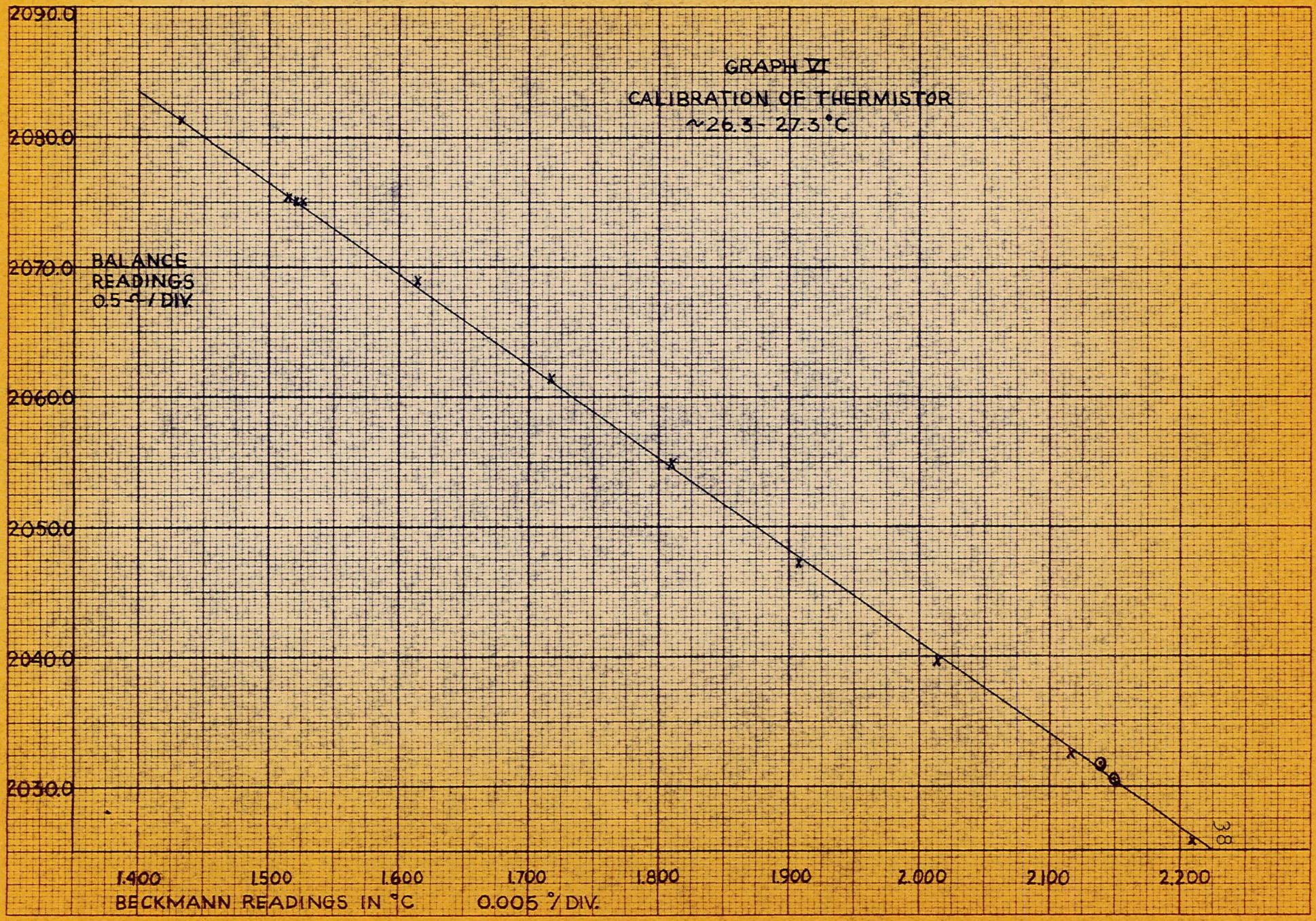
several checks were made at the various calibration points. A smooth curve obtained by using more known points would have been preferable. However, the curve does follow the general pattern obtained by Grimley (3) for his thermocouple. The second error, and probably the one that would account for the irregular deviations, is the placement of the junction of the thermocouple in relation to the capsule. An effort was made to have the junction at the mid-point of the capsule. This was accomplished by measuring the length of thermocouple lead placed in the furnace. If the leads were bent at an angle then the junction would not be at the prescribed position.

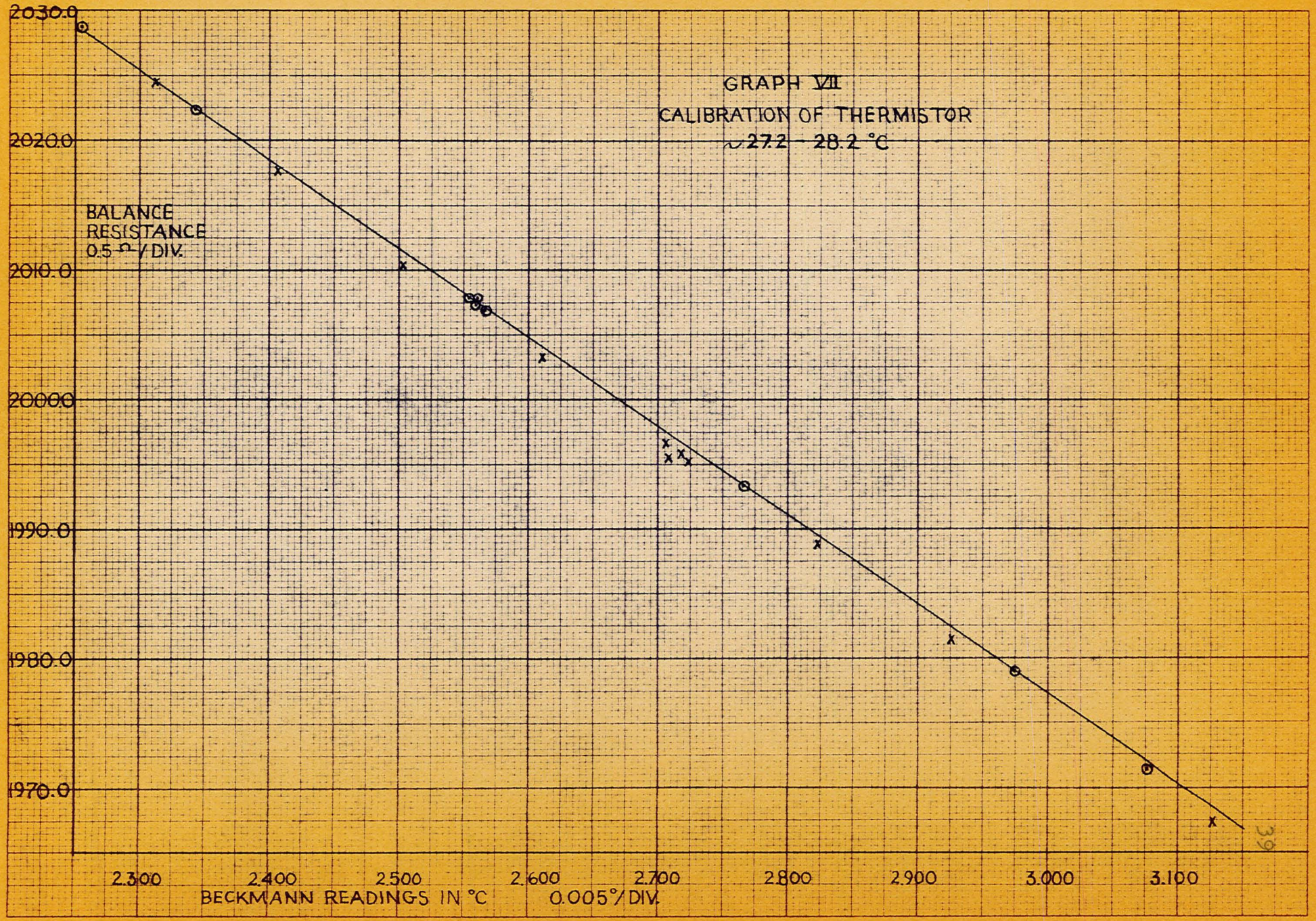
It was discovered that the constant temperature zone of the furnace was only approximately three-fourths of an inch in length at high temperatures and that the temperature in the furnace tube was quickly reduced as one moved away from this zone. By not having the thermocouple junction and the capsule exactly together at the constant temperature zone would introduce an error. A larger constant temperature zone should be obtained. This might be accomplished by placing an auxiliary heater around the outside of the central tube of the furnace.

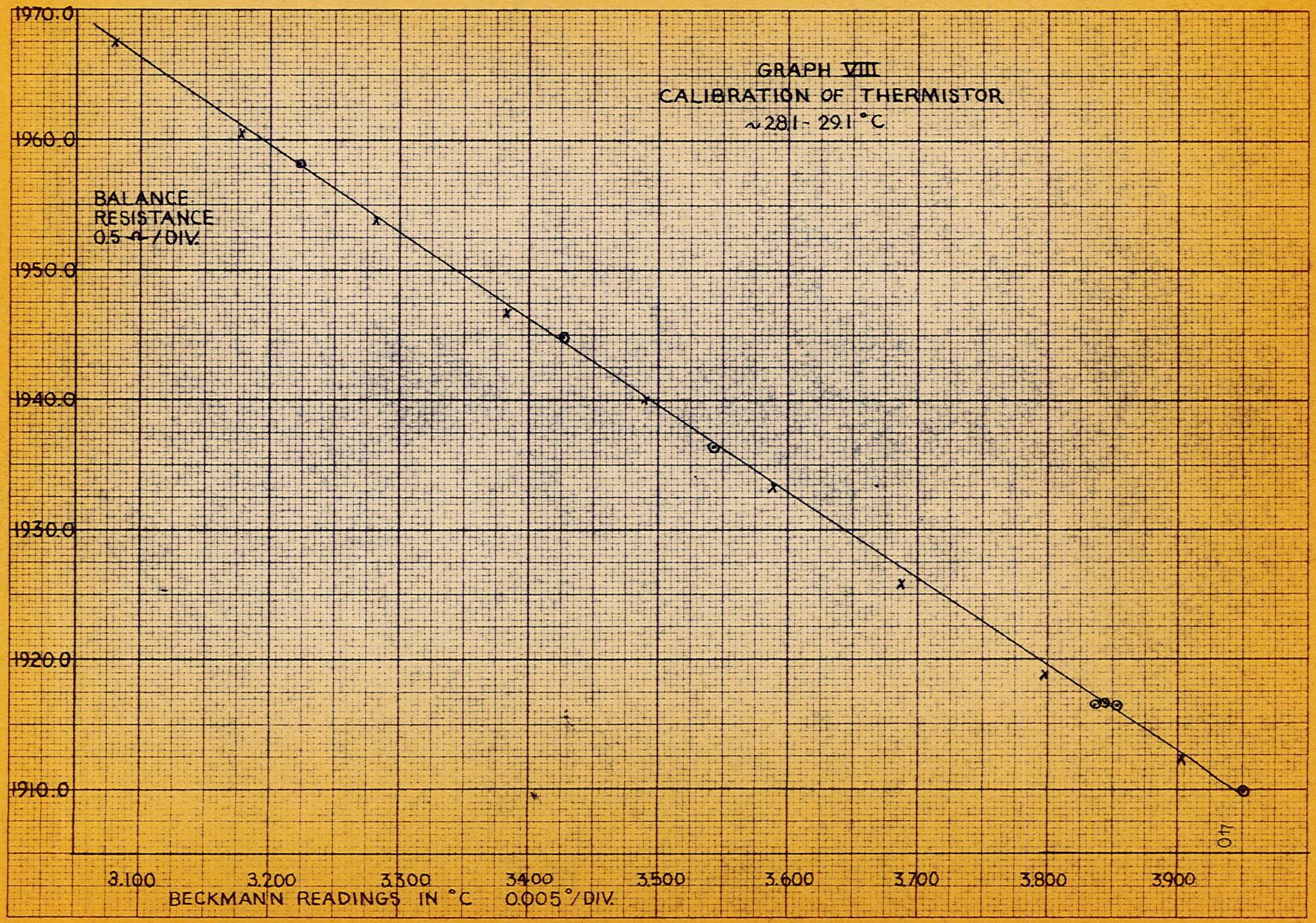
The exact values for the heat content of Al_2O_3 at high temperatures are not available. This can be seen by the difference of almost one per cent in the values obtained by the equations of Kelley (4) and Kubachewski (5).

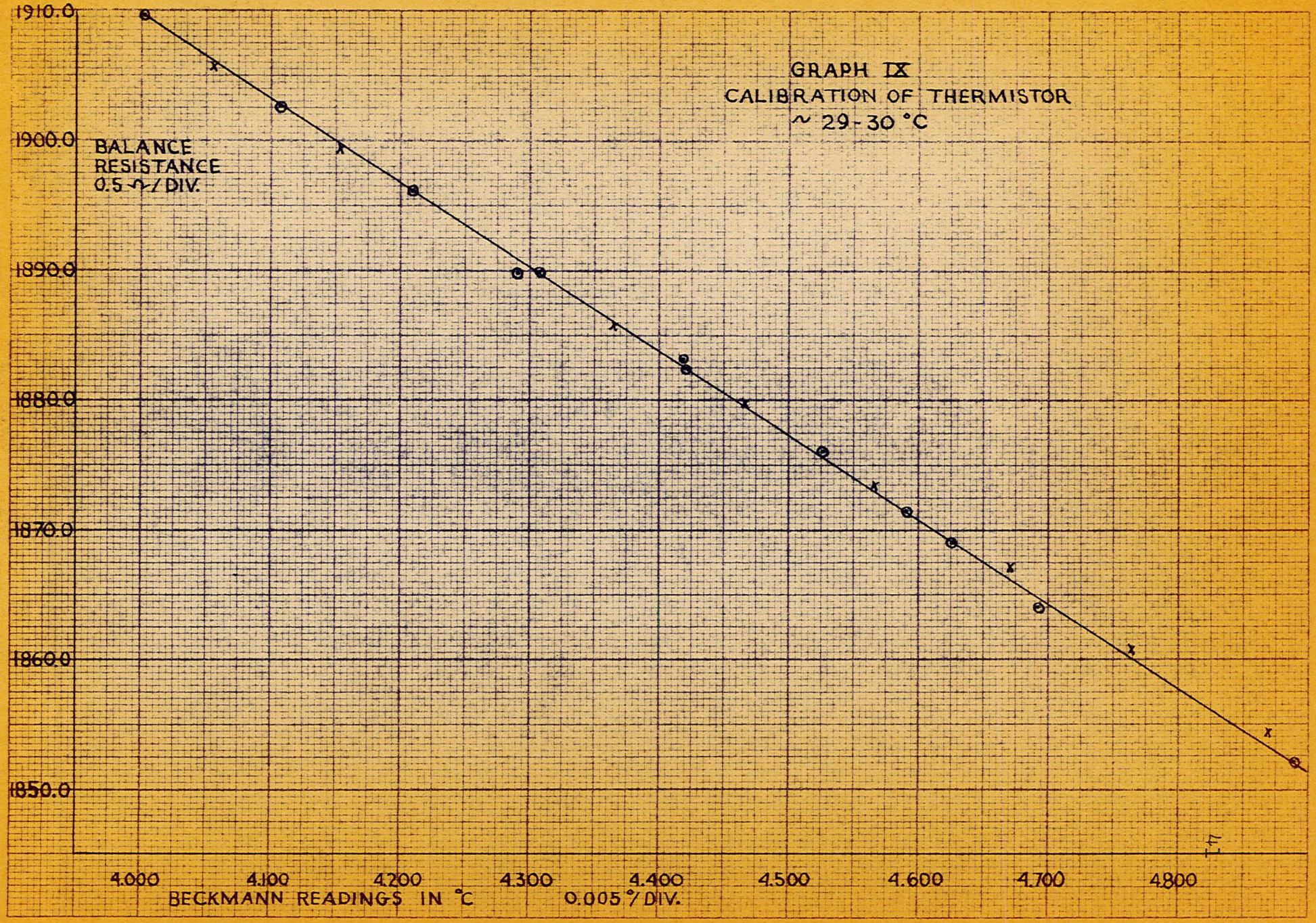

GRAPH IV
CALIBRATION OF THERMISTOR
~25 - 25.6 °C
BALANCE
RESISTANCE
0.5 Ω / DIV.
2200.0
2190.0
2180.0
2170.0
2160.0
2150.0
2140.0
⊙ VALUES OBTAINED AFTER ADDING 750 K Ω RESISTANCE
× VALUES OBTAINED BEFORE ADDING 750 K Ω RESISTANCE
0.000
0.100
0.200
0.300
0.400
0.500
0.600
BECKMANN READING IN °C
0.005 °/ DIV.






GRAPH VII
CALIBRATION OF THERMISTOR
~27.2 - 28.2 °C
BALANCE
RESISTANCE
0.5 Ω / DIV.
2030.0
2020.0
2010.0
2000.0
1990.0
1980.0
1970.0
2.300
2.400
2.500
2.600
2.700
2.800
2.900
3.000
3.100
BECKMANN READINGS IN °C
0.005°/DIV.




GRAPH IX
CALIBRATION OF THERMISTOR
~ 29-30 °C
BALANCE
RESISTANCE
0.5 Ω / DIV.
1910.0
1900.0
1890.0
1880.0
1870.0
1860.0
1850.0
4.000
4.100
4.200
4.300
4.400
4.500
4.600
4.700
4800
BECKMANN READINGS IN °C
0.005 °/ DIV.
T-77

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